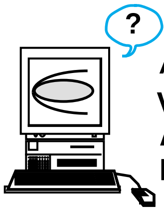

Ask Dr. ALOHA:

Vessel on Fire! Assessing Fire and Explosion Hazard

On December 21, 1993, the U. S. Coast Guard Marine Safety Office (MSO) at Charleston, South Carolina, was alerted that a fire had broken out in the machinery space of a tank barge. The barge, located near the main shipping lane leading into Charleston Harbor, was loaded with 5 million gallons of paraxylene (commonly abbreviated to “p-xylene”), a flammable solvent. The fire had not reached the barge’s cargo area. Air temperatures were in the low 50’s (°F) and the sea surface temperature was about 70°F.

Emergency responders began working to extinguish the fire on the barge. Meanwhile, to ensure the safety of the firefighters on the barge, Coast Guard marine safety officers needed a quick answer to an important question: *Could the stored p-xylene catch fire or explode if the fire were to reach the cargo tanks?* Let’s look at how the officers could get the answer that they needed.

Explosive limits

Any explosive or flammable threat to the firefighters on board the vessel would be posed not so much by the liquid p-xylene but by the vapor that had evaporated from its surface into the air space within the cargo hold. For combustion (fire) to be possible, a fuel – which can be a flammable vapor such as p-xylene – must be mixed with an oxidizing agent, such as the oxygen gas that’s always present in the atmosphere. To sustain combustion or explosion, a mixture of flammable gas and air must contain that fuel and air in certain proportions. Each flammable chemical substance has upper and lower **explosive limits** (also called **flammability limits**). These limits often are abbreviated as **UEL** and **LEL** (or **UFL** and **LFL**).

A mixture that contains too little flammable vapor (a mixture that is “too lean”) is below the LEL of the chemical, and will not burn. A mixture that contains too much fuel and too little air (a mixture that is “too rich”) is above the UEL of the substance, and also will not burn. Only a mixture with a concentration of fuel between the explosive limits can burn or explode if it is ignited. At Charleston Harbor, the Coast Guard officers needed to know whether the concentration of p-xylene vapor in the air within the barge’s cargo hold was within those limits for p-xylene.

Look for explosive limits in RIDS

What are the explosive limits for p-xylene? They are displayed (as “Lower Exp Limit” and “Upper Exp Limit”) in the Properties field on the card (in CAMEO-Mac) or screen (in CAMEO-DOS) for p-xylene in CAMEO’s RIDS database (see Figure 1). In CAMEO, explosive limits are expressed as a percentage by volume of the vapor in air. For example, CAMEO tells us that the LEL of p-xylene is about 1.1%. This means that at the LEL, there are about 1.1 volumes of p-xylene vapor in 100 volumes of air-vapor mixture. The UEL of p-xylene is 6.6%, so at the UEL, there are about 6.6 volumes of p-xylene vapor in 100 volumes of the mixture.

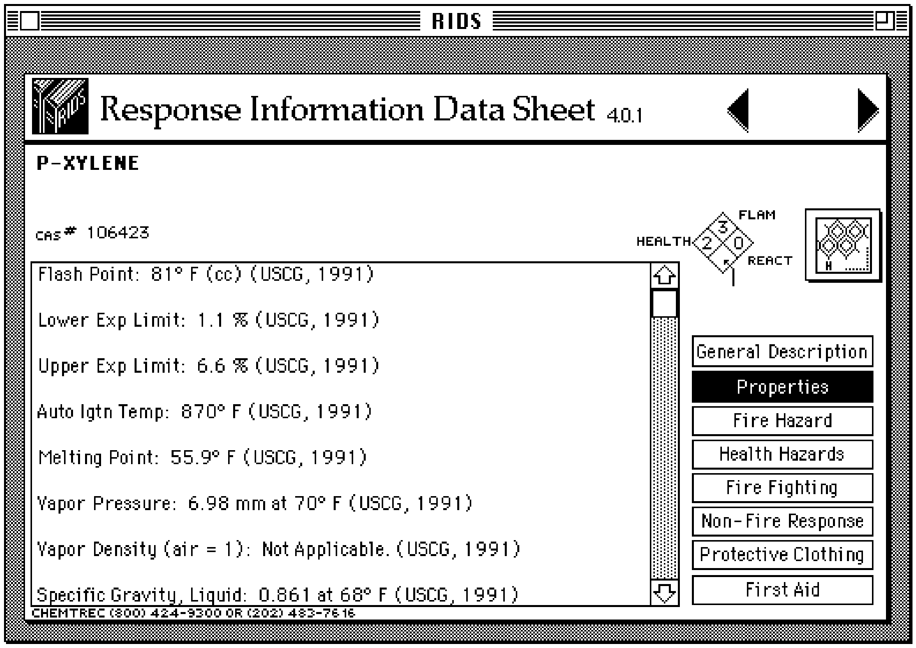

FIGURE 1. CAMEO-Mac's RIDS card for p-xylene, showing some of the chemical's physical properties.

Finding the vapor concentration

How can we find out a fuel vapor's concentration in air, so that we can see whether it lies within the explosive limits? A flammable liquid such as p-xylene, stored in a confined space such as a cargo hold, evaporates at a rate that depends on its temperature and on the amount of vapor that's already present in the air space above the liquid. Over time, the amount of evaporated vapor in that air space will stabilize at an equilibrium level called the **ambient saturation concentration**. A liquid's ambient saturation concentration reflects the magnitude of its vapor pressure compared with the vapor pressure of the air above it. If a chemical has a high ambient saturation concentration, it has a strong ability to displace air, and the concentration of the chemical's vapor in the air above the liquid will be high. If it's low, the vapor concentration will be low. This property changes with temperature: a liquid at a higher temperature will have a higher ambient saturation concentration.

You can calculate the ambient saturation concentration at a given temperature for any liquid if you have a value for the liquid's vapor pressure at that temperature and a value for the atmospheric pressure at the location. To do this, divide the vapor pressure by the atmospheric pressure, then multiply the result by 100 to obtain a value for ambient saturation concentration expressed as a percentage by volume.

You can use information from RIDS for p-xylene to make this calculation for the p-xylene on the barge at Charleston. Its temperature is likely to have been close to the temperature of the water around it, about 70°F. You can calculate p-xylene's ambient saturation concentration at that temperature, because CAMEO provides a value for p-xylene's vapor pressure at 70°F. That value is 6.98 millimeters of mercury (mmHg) (see Figure 1). Atmospheric pressure at sea level is 760 mmHg (in other common units, it's 101,325 pascals, 14.7 pounds per square inch or psi, 1 atmosphere, or 1.01 bar). So,

$$\text{ambient saturation concentration} = \frac{6.98 \text{ mmHg}}{760 \text{ mmHg}} \times 100 = 0.92\%$$

This value is lower than p-xylene's LEL of 1.1%, indicating that while the temperature within the cargo hold remains at about 70°F, the p-xylene vapor in the barge's cargo space is expected to be too lean to burn or explode.

Bear in mind that these numbers are approximate

But this ambient saturation concentration is only slightly lower than the LEL. When you interpret such a result, it's important to remember that there is uncertainty in each of the factors that go into this calculation. Neither the LEL nor the vapor pressure shown in CAMEO is an absolute, exact value. Both values were obtained by measuring samples of p-xylene in a laboratory, under specific conditions that won't be exactly duplicated in a cargo hold. Likewise, you aren't sure that the temperature in the cargo hold is exactly 70°F. If the true LEL were actually a bit lower than 1.1%, or the true temperature or vapor pressure a bit higher, the actual ambient saturation concentration of the p-xylene vapor might lie within the explosive range. What you've really learned by making your calculation is this: *the vapor concentration is at least close to the explosive range; it may be within the range.*

What if the temperature were to increase?

What if the fire were to raise the temperature of the p-xylene within the hold? The temperature at which the ambient saturation concentration of the stored p-xylene reaches the explosive range roughly corresponds to the **flash point**[1]. Like vapor pressure or LEL, flash points are determined from laboratory measurements. You can find an estimate of p-xylene's flash point in RIDS: this value, about 81°F, is displayed along with p-xylene's other properties (Figure 1). If the temperature within the cargo hold were to exceed this value, you should assume that the p-xylene vapor could catch fire or explode, if it were ignited.

[1] The flash point is defined as the lowest temperature at which the vapor above an evaporating liquid will burn when exposed to a flame.

Check Figure 2 to see how the flash point is related to temperature, ambient saturation concentration, and the LEL.

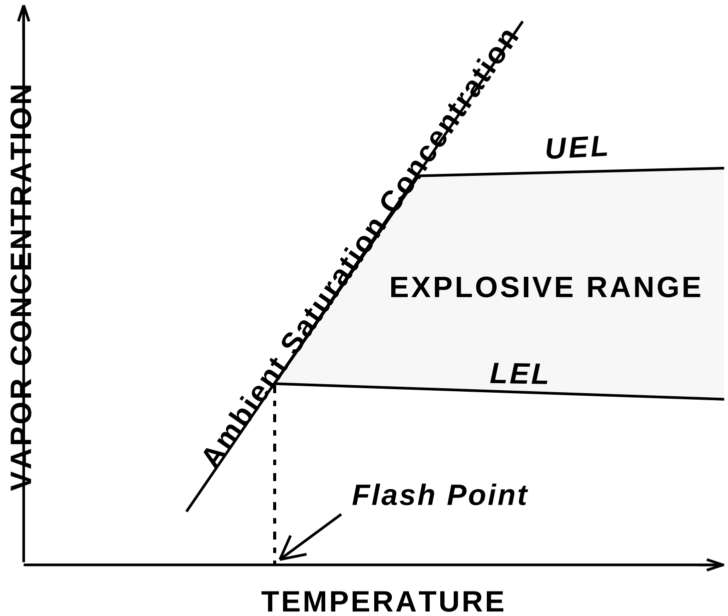

FIGURE 2. Relationships among ambient saturation concentration, LEL and UEL (the lower and upper explosive limits), and flash point.

ALOHA can help you to assess explosion hazard

ALOHA can quickly calculate ambient saturation concentration of a stored liquid for you. Once you've selected a chemical and its location and entered atmospheric conditions, ALOHA automatically displays the chemical's ambient saturation concentration (it's not necessary to set a source or calculate a footprint). ALOHA's value for ambient saturation concentration is for the selected chemical, in this case p-xylene, at the air temperature that you enter. The officers at Charleston would need to enter the air temperature within the cargo hold, not the air temperature outside the barge. ALOHA would assume the p-xylene to be at the same temperature as the air in the hold.

To find the ambient saturation concentration of the p-xylene on the barge at Charleston, just start ALOHA, choose **Chemical...** from the **SetUp** menu, then type "x" to quickly find "p-xylene" in the chemical list[2]. Select p-xylene, then choose **User Input...** from the **Atmospheric** menu under the **SetUp** menu. Enter an air temperature of 70°F; you can enter any values that you'd like for all other weather conditions, because ALOHA doesn't use them to calculate ambient saturation concentration (your choices of location and time of day likewise won't

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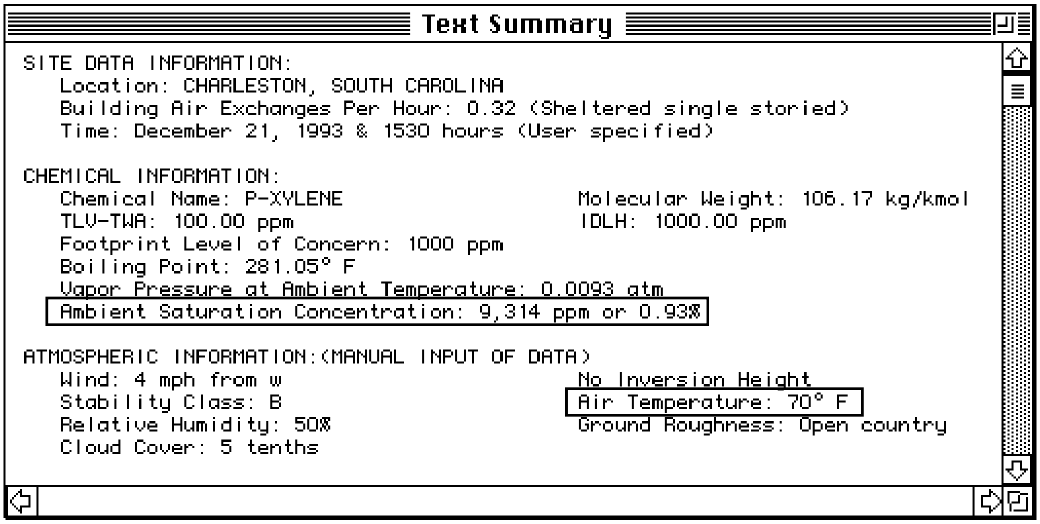
[2]ALOHA's chemical list is alphabetical, with prefixes to chemical names, such as p- or 1-, ignored.

affect this calculation). You'll see ALOHA's estimate for ambient saturation concentration, 0.93%, on the Text Summary window (Figure 3).


Text Summary

SITE DATA INFORMATION:
Location: CHARLESTON, SOUTH CAROLINA
Building Air Exchanges Per Hour: 0.32 (Sheltered single storied)
Time: December 21, 1993 & 1530 hours (User specified)

CHEMICAL INFORMATION:
Chemical Name: P-XYLENE
Molecular Weight: 106.17 kg/kmol
TLV-TWA: 100.00 ppm
IDLH: 1000.00 ppm
Footprint Level of Concern: 1000 ppm
Boiling Point: 281.05° F
Vapor Pressure at Ambient Temperature: 0.0093 atm
Ambient Saturation Concentration: 9,314 ppm or 0.93%

ATMOSPHERIC INFORMATION:(MANUAL INPUT OF DATA)
Wind: 4 mph from w
No Inversion Height
Stability Class: B
Air Temperature: 70° F
Relative Humidity: 50%
Ground Roughness: Open country
Cloud Cover: 5 tenths

FIGURE 3. ALOHA's Text Summary window, showing the ambient saturation concentration of p-xylene at 70°F.

If no flash point is available in CAMEO for a chemical you're concerned about, you can use ALOHA to quickly estimate it. By successively running ALOHA, each time changing only air temperature, then checking the value for ambient saturation concentration displayed in the Text Summary window, it's possible to find the approximate flash point, since it's about the temperature at which the ambient saturation concentration equals the LEL. For the p-xylene at Charleston, you could enter 70°F as your first air temperature value, then increase the temperature by several degrees and rerun the model until you see that the value for ambient saturation concentration, shown on the Text Summary screen, reaches the LEL. If you do this, you'll find that ALOHA predicts that at about 75°F, ambient saturation concentration reaches 1.10%, the LEL. This value is close to the flash point value of 81°F displayed in CAMEO for p-xylene. The fact that the values are a few degrees apart indicates not that CAMEO or ALOHA is "wrong," but that any flash point estimate is approximate, not exact.

It's also possible to use ALOHA to find the approximate temperature at which the ambient saturation concentration would reach the UEL (this temperature is called the upper flash point). For p-xylene, this temperature is about 138.5°F (Figure 4). If the temperature in the hold were to substantially exceed this value, the concentration of the p-xylene vapor in the cargo hold would be too rich to burn or explode.

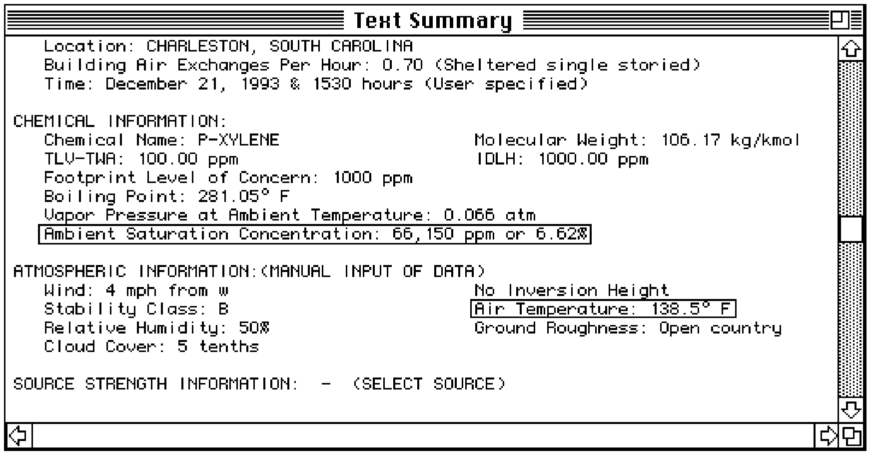


FIGURE 4. ALOHA’s Text Summary window, showing the ambient saturation concentration of p-xylene at 138.5°F.

Epilogue

At Charleston, the firefighters were able to extinguish the fire before it reached the cargo hold; the barge was towed back to the harbor for repair, and its cargo was transferred to another vessel without problem. But flammable liquids such as p-xylene are transported daily on the nation’s waterways and highways. When an accident happens, as at Charleston Harbor, CAMEO and ALOHA can provide information to help you to quickly assess fire and explosion hazards.

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